Transannularly Bridged Di-μ_2-thiotetraborane(10). Dynamics, *cis–trans*-Isomerism, Reversible Rearrangement: Bis(diboranyl) 'Butterfly' Structure

Herbert Binder,* Paraschos Melidis, Serdar Söylemez and Gernot Heckmann

Institute of Inorganic Chemistry, University of Stuttgart, Pfaffenwaldring 55, D-7000 Stuttgart 80, Germany

B_4H_{10} reacts with bifunctional thiols to give transannularly bridged $H_2(\mu_2)_2S_2RBH(B_2H_5)$ which exist as *cis–trans* isomers; on cooling these compounds rearrange to *cis–trans* $H_2B(\mu_2)_2S_2RB_3H_6$.

Tetraborane(10) reacts with carboxylic acids by splitting off H_2, displacement of 'BH_3', and coordination of the carboxylate group to form chelate-stabilized compounds of the type B_3H_6X, where $X = RCO_2$.[1,2] It was shown that the primary reaction step is not initiated by the acidic H atom of the CO_2H group but by the carbonyl group. We now find that the B_4H_{10}–thiol system follows a similar reaction path. We report here on results of reactions between B_4H_{10} and bifunctional thiols. The reactions proceed through unstable addition compounds and yield by H_2 loss the title compounds *via* reaction (1).

$$B_4H_{10} + R(SH)_2 \rightarrow B_4H_8(S_2R) + 2\,H_2 \qquad (1)$$

1a; R = CH_2
b; R = $(CH_2)_2$
c; R = $(CH_2)_3$
d; R = 1,2-C_6H_4

The ^{11}B NMR spectra of **1a–d**† show at room temperature two series of signals consisting of a doublet, a triplet and a sextet (1 : 1 : 2) indicative of two isomers (Fig. 1). The sextets, which exhibit considerably smaller $^1J(^{11}B^1H)$ coupling con-

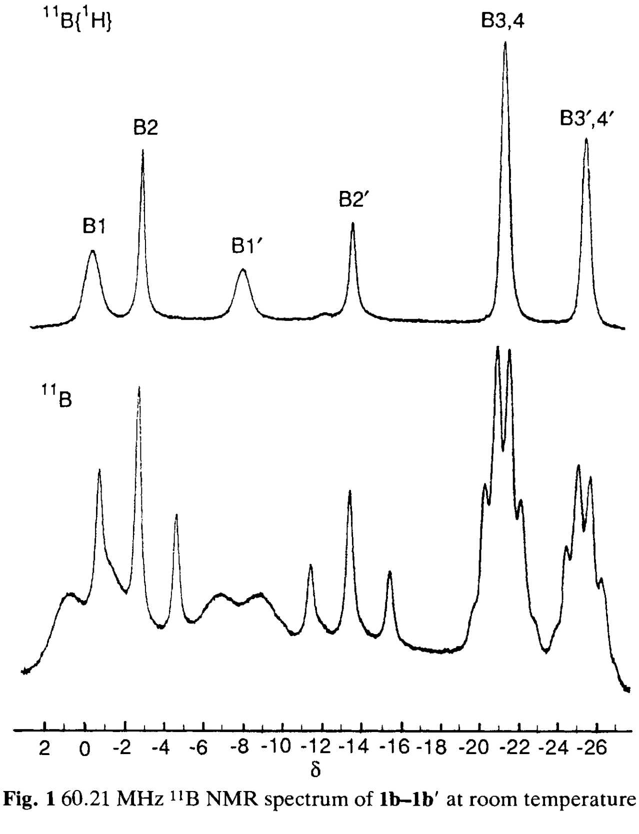

Fig. 1 60.21 MHz ^{11}B NMR spectrum of **1b–1b′** at room temperature

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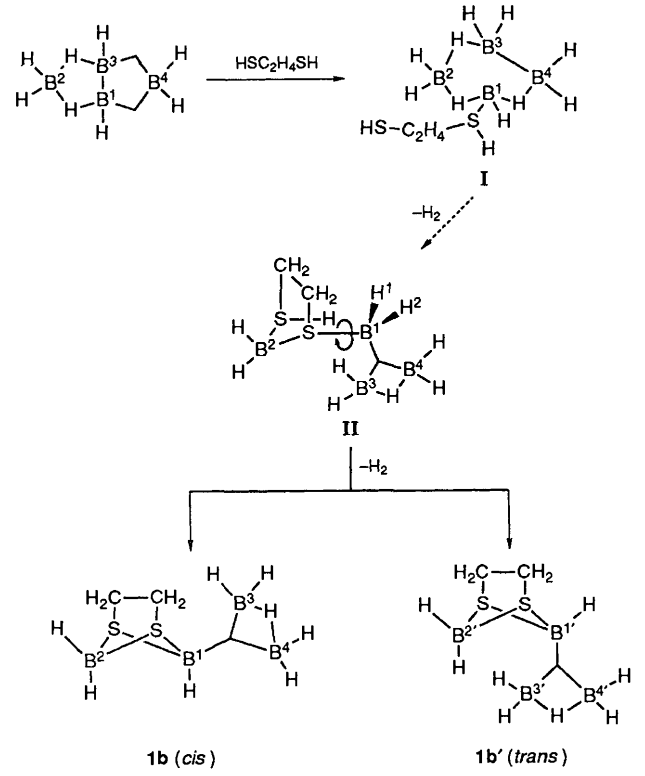
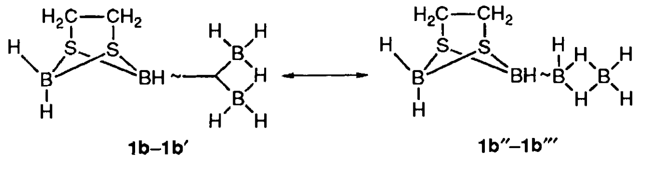
† *Experimental data*: The ^{11}B, ^1H and ^{13}C NMR spectra were recorded at 64.210, 200.132 and 50.323 MHz.

Preparation of **1a–d**: the appropriate dithiol **1a–d** was added at 15 °C to a solution of B_4H_{10} (5.5 mmol) in CH_2Cl_2[2] (0.4 mol dm^{-3}). The reaction is complete after 30 min. Excess of B_4H_{10} was removed by evaporation to half bulk. The remaining reaction mixture was examined spectroscopically. The isomer ratios were determined from the clearly separated sextets of the ^{11}B NMR spectrum at room temperature. All isomers with the higher chemical shift (see Fig. 1) always appear with a lower intensity: **1a**:**1a′** 60:40; **1b**:**1b′** 60:40; **1c**:**1c′** 70:30; **1d**:**1d′** 70:30.

Side products: δ (^{11}B): **1a**: −16.7 (t), $[CH_2(SBH_2)_2]_2$[6] (5%), −19.6 (t), −26.7 (m) (5%), not identified; **1b**: none; **1c**: −14.5 (t) (5%), −18.5 (t) (5%), −25.5 (m) (10%), −29.5 (m) (10%), not identified; **1d**: 58.0 (d) $C_6H_4S_2BH$ (10%), −25.0 (m) (3%), not identified.



Scheme 1 Reactions starting with the B_4H_{10} 'butterfly' structure and leading to the *cis–trans* isomers **1b–1b′** with the bis(diboranyl) structure



Scheme 2 Dynamics of the B_2H_5 in **1b–1b′** or **1b″–1b‴**

stants compared with the B–H coupling constants of the doublets or triplets, are associated with B_2H_5 groups in which all H atoms on the NMR time scale are subject to a rapid dynamic process. The structure of the reaction products **1a–d** cannot be derived from the 'butterfly' structure of B_4H_{10} by these parameters; a terminal or bridge H substitution on this structure should lead to a different shape of the ^{11}B NMR spectrum.

The ^{11}B NMR spectrum is consistent, however, with a bis(diborane) structure of B_4H_{10}[3,4] in which the opposite H bridge positions are substituted transannularly by a dithio group (Scheme 1). The primary reaction step is the adduct formation;‡ the succeeding H_2 split-off, rearrangement (μ_2-S bridge formation), and renewed addition of the second SH group at B^2 yields the intermediate compound **II** with the opening of a H bridge. Compound **II** is the precursor for the *cis–trans* isomers **1b–1b′**. Rotation of the B_3H_7 group around the B–S bond in **II** allows the reaction of H^1 and H^2 with the SH group with H_2 cleavage, whereby **1b** or **1b′** are formed (*cis–trans* refers here to the position of the transannular RS_2 bridge opposite the B_2H_5 group). The dynamics of the B_2H_5 group can be illustrated by a rapid oscillation between the two limiting forms **1b–1b′** and **1b″–1b‴** (Scheme 2).

With **1b″–1b‴**, we succeeded in preparing a derivative of the hypothetical bis(diborane), a valence isomer of B_4H_{10}.

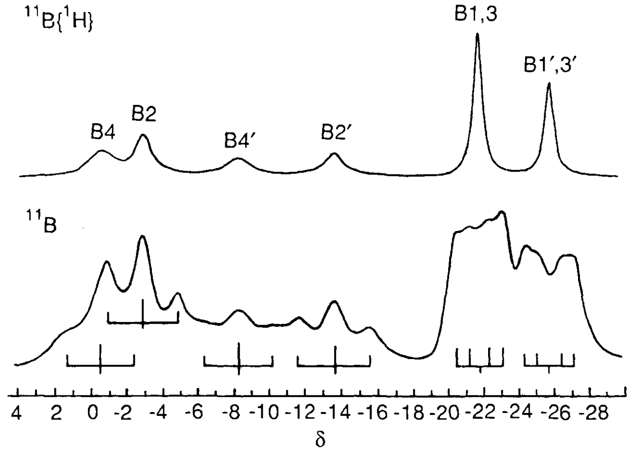
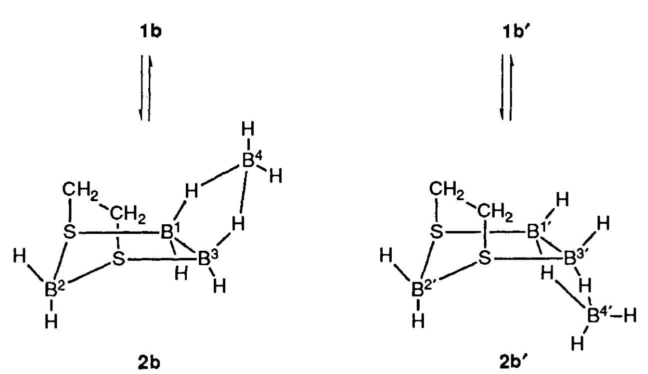


Fig. 2 60.21 MHz ^{11}B NMR spectrum of **2b–2b′** at −50 °C



Scheme 3 Reversible rearrangement of the bis(diboranyl) structure of **1b–1b′** into the 'butterfly' structure **2b–2b′**

The rapid structural change is related to magnetic equivalence of the two boron atoms B^3,B^4 and the five H atoms. The reorientation of the B_2H_5 group can be interpreted as a pseudorotation. From the ^{11}B NMR data it is not possible to differentiate between the *cis–trans* isomers. In order to find out whether one of the limiting structures is rigid at low temperatures, we recorded ^{11}B NMR spectra as a function of temperature. Surprisingly, none of the limiting forms could be detected. Instead, we found that an intramolecular rearrangement occurred upon cooling resulting in two new *cis–trans* isomers.

A temperature-dependent equilibrium is reached which at −50 °C lies completely on the side of the new isomers. The ^{11}B NMR spectrum shows two new multiplet series at −50 °C which contain two triplets each and a doublet of doublets (1 : 1 : 2), as shown in Fig. 2.

These multiplets clearly indicate the transannularly bridged 'butterfly' structure of B_4H_{10} which appears in a *cis* and *trans* form (Scheme 3).

The doublets of doublets result from the coupling of the boron atoms B^1 and B^3 or $B^{1'}$ and $B^{3'}$ with a terminal and a bridging H atom. The triplets are caused by the coupling of the boron atoms B^2 and B^4 and $B^{2'}$ and $B^{4'}$ with two terminal H atoms each; the couplings of the two bridging H atoms with B^4 and $B^{4'}$ are not resolved. The rearrangement leads to a larger ring: the four-membered ring B_2S_2 in **1b–1b′** enlarges to a five-membered ring B_3S_2 in **2b–2b′**. An analogously structured derivative is the recently described compound $H_2B(\mu_2\text{-}NMe_2)_2B_3H_6$,[5] the only known B_4H_{10} derivative with bridge substituents. On warming to room temperature, the same type of spectrum as in Fig. 1 appears again. This is indicative of a reversible rearrangement, *i.e.*, a reversible ring expansion–ring contraction process. Heating to 90 °C leads to no further change. The experimentally demonstrated rearrangement of the bis(diboranyl) structure into the 'butterfly' structure

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‡ The addition compound $Bu^tSH{\cdot}B_4H_{10}$ was detected by ^{11}B NMR spectroscopy: δ −7.2, −35.8 (3 : 1); the compound undergoes a dynamic process.

1b–1b′ → **2b–2b**′ is an indication that the theoretically calculated transformation of the hypothetical valence isomer $(B_2H_5)_2$ into the known 'butterfly' structure of B_4H_{10} is realistic.

The proof of the structure and the characterization of the compounds **1a–d** is based on ^{11}B, ^{13}C and ^{1}H NMR spectroscopy as well as mass spectrometric investigations.§ After removing the solvent, partial polymerization occurs; crystalline products could not be obtained yet. The reaction products of longer-chain dithiols, beginning with butane-1,4-dithiol, show only broad, unresolved signals in the ^{11}B NMR spectrum; no monomers could be identified mass spectrometrically; a similar situation exists with **1c** under solvent-free conditions.

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§ *Spectroscopic data*: (numbering of the atoms according to Fig. 1 and Fig. 2) ^{11}B NMR (CD_2Cl_2): **1a** (302 K): δ −8.9 (d, J_{BH} 100 Hz, B^1H), −12.2 (t, J_{BH} 130 Hz, B^2H_2), −23.6 (sex, J_{BH} 35 Hz, $B^2B^4H_5$); **1a**′ (302 K): δ −9.7 (d, J_{BH} 92 Hz, $B^{1\prime}H$), −14.4 (t, J_{BH} 100 Hz, $B^{2\prime}H_2$), −23.9 (sex, J_{BH} 35 Hz, $B^{3\prime}B^{4\prime}H_5$); mass spectrometry **1a–1a**′ *m/z*: 126 ($\{M - 4H\}^+$, 22%); ^{11}B NMR (CD_2Cl_2): **1b** (302 K): δ −0.1 (d, J_{BH} 118 Hz, B^1H), −2.6 (t, J_{BH} 126 Hz, B^2H_2), −21.2 (sex, J_{BH} 39.6 Hz, $B^3B^4H_5$), **1b**′ (302 K): δ −7.8 (d, J_{BH} 121.5 Hz, $B^{1\prime}H$), −13.4 (t, J_{BH} 126.4 Hz, $B^{2\prime}H_2$), −25.3 (sex, J_{BH} 37.8 Hz, $B^{3\prime}B^{4\prime}H_5$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): **1b** (302 K): δ 34.05 (CH_2), **1b**′ (302 K): δ 32.95 (CH_2); ^1H NMR (CD_2Cl_2): **1b–1b**′ (302 K): δ 0.2–4.2 (broad overlapping multiplets, BH signals), **1b** (302 K): δ 2.97, 2.67 [AB-system, $^2J_{HH}$ 7.1 Hz, (CH_2)], **1b**′ (302 K): δ 2.85 (s, CH_2); mass spectrometry: **1b–1b**′ *m/z*: 140 ($\{M - 4H\}^+$, 70%); ^{11}B NMR (CD_2Cl_2): **2b** (220 K): δ −0.5 (t, J_{BH} 113 Hz, B^4H_2), −2.8 (t, J_{BH} 128 Hz, B^2H_2), −21.7 (dd, J_{BH} 120.4 Hz, $B^1H_tB^3H_t$, J_{BH} 42 Hz, $B^1H_bB^3H_b$); **2b**′ (220 K): δ −8.7 (t, J_{BH} 132 Hz, $B^{4\prime}H_2$), −13.6 (t, J_{BH} 117 Hz, $B^{2\prime}H_2$), −25.8 (dd, J_{BH} 140 Hz, $B^{1\prime}H_tB^{3\prime}H_t$, J_{BH} 35 Hz, $B^{1\prime}H_bB^{3\prime}H_b$).